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(54) Title: CONCENTRATED SURFACTANT COMPOSITIONS

(57) Abstract

Aqueous, mobile, concentrated, amphoteric surfactant compositions consist substantially of: 5 % to 45 % by weight water, at least 36 % to 70 % by weight of amphoteric surfactant and 5 to 45 % of a water miscible, non-surfactant organic solvent, said compositions being in the "G" or "L_1" phase.

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Concentrated Surfactant Compositions

The present invention relates to novel, concentrated aqueous surfactant compositions, in particular to amphoteric surfactant compositions which are mobile or pumpable at high concentrations of active ingredient. Such compositions are prepared in the presence of a phase modifier, thus allowing the preparation of such compositions over a wider range of active concentrations than has hitherto been possible. More specifically, the present invention relates to a novel method for the production of particular concentrated amphoteric surfactant compositions, especially betaines and fatty imidazoline derivatives, wherein preparation of such surfactants or surfactant compositions utilises a non-surfactant organic solvent as a phase modifier.

The preferred betaines according to the present invention, are N-carboxymethylated derivatives of tertiary amine intermediates possessing at least one fatty alkyl chain e.g. cocoamido propyl betaine (CAPB), sulphobetaines, phosphobetaines, and hydroxysulphobetaines, and N-carboxymethylated derivatives of amidoamines e.g. produced by the hydrolysis of imidazolines and especially of imidazolines having an alkyl and a hydroxyalkyl chain e.g. N-carboxymethylated lauric hydroxyethyl imidazoline (CLHI).

TECHNICAL BACKGROUND

Amphoteric surfactants incorporate electropositive and electronegative elements in the same molecule, allowing for the formation of salts in either acidic or alkaline conditions. Amphoteric surfactants are generally gentle on the skin and eyes, exhibit low toxicity, and are very effective as mild surfactants.

Furthermore, developments in the detergent and personal hygiene product areas have become increasingly focused on derivatives of naturally-occurring raw materials, such as natural fats and oils, because of the environmental and toxicological advantages such derivatives offer over more conventional raw feedstocks.

Surfactant compositions are prepared and sold for a wide variety of industrial and domestic applications. They are often required in a fluid form, and it is therefore often desirable that they should contain as high a proportion of active material as possible, whilst retaining mobility in order to reduce the costs of storage and transport.

Where the surfactant composition has a melting point below, or only slightly above ambient temperature it is sometimes possible to supply the surfactants in the form of an anhydrous composition, or a composition containing up to about 5% of water, respectively. In the latter case the trace of water appears to act as a melting point depressor.

However, in the case of surfactant compositions which are solid at temperatures above about 25°C, it has often been impossible to obtain a fluid composition at concentrations above about 30 to 40% by weight of active ingredient, depending on the nature of the composition. Small amounts of water up to about 10% do not depress the melting point sufficiently, while larger amounts, sufficient to cause a phase change result in the formation of a rigid gel, rather than a fluid solution. It has generally been found that as the total concentration of active ingredient in a dilute solution approaches a critical level, which is usually about 30% by weight, or in the case of some mixtures may be somewhat higher, e.g. up to about 55% by weight, the viscosity of the

solution begins to rise, causing difficulty in the preparation and handling of the compositions. At or around a critical concentration level the solution sets into an immobile gel, or phase separation occurs.

It is sometimes possible to increase the concentration of active ingredient stably incorporated into a solution by the addition of viscosity modifiers or cosolvents. These additives act as thinners, both lowering the viscosity of the solution and inhibiting the formation of gels, so that higher concentrations may be attained. However such cosolvents, for example alcohols, may be effective in producing substantial increases in the attainable concentration of the surfactant composition having an acceptable viscosity, only when they are present in such large amounts that may adversely affect the properties of the product for many of its desired end uses and/or increase the cost of the product.

It is known (see for example "Advances in Colloid Interface Science" 1 (1967) 79-110 pp. 82-83) that many surfactant compounds or mixtures are capable of forming highly viscous, non-pumpable liquid crystal phases. Some of these compounds or mixtures form a phase of relatively low viscosity compared with other liquid crystal phases, which is usually referred to as the "G" or "lamellar phase" and which forms only within a specific concentration range. The "G" phase is a pumpable fluid which is formed over a narrow range of concentrations which range usually lies between 40% and 85% by weight of active ingredient and is characterised by a lamellar structure in which the surfactant molecules are associated to form plates of indefinite size separated by planes of water molecules. However, in the few cases of the amphoteric surfactants where the existence of a "G" phase has been reported, it can only be formed at elevated temperatures, or over a concentration range so narrow as to be of no practical use.

It is known in the art that certain surfactants of commercial value e.g. some ammonium alkyl sulphates and some olefin sulphonates form "G" phases at ambient temperature, and are now prepared in a fluid form at very much higher concentrations than could previously have been achieved. (See for example GB Patent No. 1,488,352.)

Mixtures of surfactants tend to form fluid "G" phases at relatively low temperatures compared with the typical minimum temperatures at which aqueous solutions of most individual surfactants (which are capable of forming "G" phases) can exist in such a phase. Usually mixtures can be obtained as a fluid "G" phase at ambient temperatures or by slight warming, whereas individual surfactants are typically much more difficult to obtain as "G" phases.

Typically, when a composition of the surfactants according to the present invention is prepared in aqueous solutions of increasing concentration, the molecules are first found to associate in spherical clusters (micelles), which with increasing concentrations become rod-like. With increasing concentration, the micelles become more crowded, resulting in a rise in the viscosity of the solution and, with the great majority of cases, said micelles eventually lengthening to form a regular hexagonal array of cylindrical surfactant micelles in an aqueous medium, usually referred to as the rigid "M_1" liquid crystal phase. If the concentration of a surfactant in the "M_1" phase is progressively increased, a phase change occurs to produce either a hydrated solid phase, or, in the case of certain surfactant mixtures containing one or more surfactants of this invention, to convert the M_1 phase progressively to a fluid "G" phase until a viscosity minimum is reached. Further increasing the concentration of the "G" phase results in an increase in viscosity, and ultimately to a further phase change, producing either an hydrated solid or a second immobile liquid crystal phase (the M_2 phase) which resembles

the M_1 phase in structure, but wherein the structure is inverted - i.e. with water as the internal phase and the surfactant as the continuous phase.

The foregoing description is however somewhat simplified. The term "hydrated solid phase" has been used broadly to include those systems which comprise suspensions of solid or immobile gel phases in one or more viscous or gel phase to provide a more or less rigid material usually having a granular appearance under a polarising microscope. No one surfactant has been found which will form all of the various liquid crystal phases.

The following terms may require explanation or definition in relation to the different phases discussed in this specification: "Optically isotropic" phases do not tend to rotate the plane of polarisation of plane polarised light. If a drop of sample is placed between two sheets of optically plane polarising material whose planes of polarisation are at right angles, and light is shone on one sheet, optically isotropic samples do not appear substantially brighter than their surroundings when viewed through the other sheet. Optically anisotropic materials however appear substantially brighter. Optically anistropic mesophases typically show characteristic textures when viewed through a microscope between crossed polarisers, whereas optically isotropic phases usually show a dark, essentially featureless continuum.

Newtonian liquids have a viscosity which is independent of shear. For the purposes of this specification, liquids are considered Newtonian if the viscosity does not vary substantially at shear rates up to 1000 sec^{-1}.

L_1-phases are mobile, optically isotropic, and typically Newtonian liquids which show no texture under the polarising microscope. Electron microscopy is capable of resolving texture only at very high magnifications. The viscosity of an L_1-phase is usually low, but may rise significantly as the concentration approaches the upper phase boundary. This is believed to reflect a change in the shape of the micelles from spherical to prolate.

G-phases are pourable, thixotropic, anisotropic products. They are typically viscous-looking, opalescent materials with a characteristic "smeary" appearance on flowing. They form characteristic textures under the polarising microscope.

M-phases are typically immobile, anisotropic products resembling waxes. They give characteristic textures under the polarising microscope.

The "G" phase or "L_1" phase can be located very rapidly and easily, using standard laboratory equipment, by placing a sample of the test composition (at the active concentration estimated to produce a "G" or "L_1" phase) on a slide on the block of a heated stage microscope. Examination between crossed polarisers will reveal in which phase the sample is present. The various phases each have a characteristic appearance which is easily identified by comparison, for example with the photographs of typical liquid crystal phases in the classic paper by Rosevear, JAOCS Vol 31 P 628 (1954) or in J. Colloid and Interfacial Science, Vol 30 No 4 P 500.

If the mixture is in a M_1 phase, water may be allowed to evaporate from the edges of the sample under the cover disk and any phase resulting changes observed. If an M_2 phase or hydrated solid is present water may be added around the edge of the cover disks and allowed to diffuse into the

composition, both of which may alter the active concentration of the sample under investigation, by an amount sufficient to produce a "G" phase. If no "G" phase is located in this way samples may be heated progressively on the block and the operation repeated.

The term "active concentration" as used herein refers to the total concentration of surface active material in the total aqueous surfactant composition.

THE PROBLEM

A particular requirement exists for mobile, pumpable concentrated aqueous amphoteric surfactant compositions, in order to reduce transport and storage costs. This need is increased by the growing trend towards the use of amphoteric surfactant compositions in applications where mildness is considered an important feature of the surfactant.

A further requirement exists for the production of amphoteric surfactants "in situ" to produce a mobile, pumpable, concentrated surfactant composition at high concentrations of active ingredient that hitherto were unattainable.

Previously at the levels of active ingredients described according to the present invention, such compositions would typically have been an immobile gel (M_1-phase) with poor dilution characteristics, causing significant problems in preparation and handling.

PRIOR ART

Amphoteric surfactant compositions, for example CAPB and CLHI, have hitherto only been obtainable as liquid compositions at concentrations of less than approximately 30% w/w active ingredient, based on the total weight of the

composition. At more commercially desirable concentrations (eg. up to about 50% w/w active ingredient) the compositions are typically sticky, very viscous or immobile, and difficult to handle, requiring where possible expensive spray-drying in order to achieve a commercially acceptable powdered product. However, because of the finely divided nature of the powder, this also presents handling difficulties and, moreover may entail health risks.

THE INVENTION

We have discovered that by preparing solutions of individual surfactants in the presence of small amounts of water soluble non-surface active solvent at the particular active concentration corresponding to the formation of the "G" phase or "L_1" phase we have been able to obtain pumpable, mobile surfactant compositions at active concentrations which are in excess of those that have hitherto been attainable. This gives rise to substantial savings in the cost of transporting and storing the products.

Generally, and unexpectedly, dilution of the concentrated compositions back to conventional concentrations in many instances presents no particular technical difficulties with the compositions exhibiting little or no tendency to form an intermediate gel phase on addition of sufficient water to effect such dilution.

We have further discovered that by controlling the non-surfactant organic solvent:water ratio in the reaction medium it is possible to produce concentrated aqueous surfactant compositions in either an "L_1" phase or "G" phase, both phases being mobile and pumpable, at concentrations of active ingredients that hitherto in the absence of the aforementioned solvent, typically produced 'M_1' phase compositions.

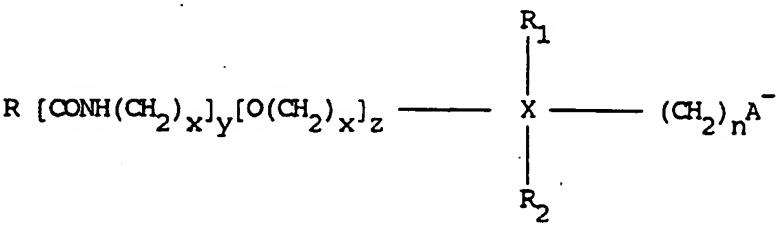
Although the ratio of solvent:water required to obtain either an "L_1" or "G" phase composition will vary according to the particular active ingredients in question "L_1" phase composition is more likely to be formed in a reaction medium having an excess of water, and a "G" phase composition is more likely to be formed in a reaction medium having an excess of solvent. However, this is only a generalisation, the exact ratio for the reaction medium being dependent upon the active ingredients comprising said surfactant system.

STATEMENT OF INVENTION

The present invention provides aqueous, mobile, concentrated, amphoteric surfactant compositions, consisting substantially of at least 5% and not more than 45% by weight of water, preferably not more than 40%; at least 30% by weight of amphoteric surfactant, preferably 35 to 70%; and 5 to 45% of a water-miscible, non-surfactant organic solvent, wherein said composition is a "G" phase and the concentration of surfactant in said composition corresponds to that at which the composition can exist, at least predominantly, in the "G" phase.

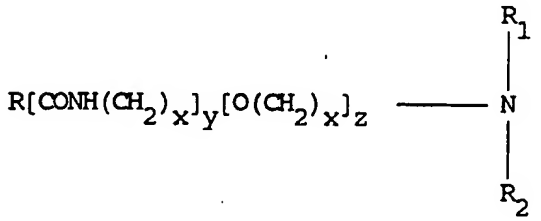
The present invention further provides aqueous, mobile, concentrated amphoteric surfactant compositions, consisting essentially of at least 5% and not greater than 65% by weight of water, preferably 10% to 60%; at least 25% by weight of amphoteric surfactant, preferably 30% to 70%; 5% to 45% of a water miscible, non-surfactant organic solvent, wherein said composition is an "L_1" phase.

The amphoteric surfactants may for example comprise a compound of the formula:-



Wherein R is an alkyl, alkenyl, alkylamidoalkyl, alkenylamidoalkyl, alk(en)yl polyoxyalkylene or alkaryl group having in each case a C_{7-} C_{22} Straight or branched chain alk(en)yl group or may be combined with R_1 to form a cyclic group,, x = 0 to 8, y = 0 or 1, z = 0 to 20, R^1 is H or a C_1-C_6 straight or branched chain alkyl, alkenyl or hydroxyalkyl group or may be combined with R or R_2 to form a cyclic group, R_2 is H or a C_1-C_6 straight or branched chain alkyl, alkenyl or hydroxyl group, or may be absent or may be combined with R_1 to form a cyclic group, X is nitrogen or phosphorus n is from 1 to 3 and A is COO^-, SO_3^- or PO_3H^-.

The composition of the present invention may be prepared by reacting a secondary or tertiary amine:-

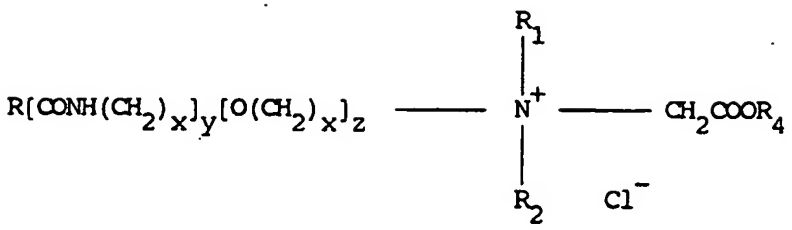


wherein R, R_1 and R_2 are as hereinabove defined, with a carboxymethylating agent in the presence of the appropriate proportions of the non-surfactant water-miscible solvent and water.

Typically the amphoteric surfactant may be a derivative of a fatty imidazoline such as (for example) an N-hydroxyethyl fatty alkyl imidazoline.

Compositions of our invention may be prepared by:

(i) adding a chloroacetate ester to a secondary or tertiary amine to produce an ester of formula:



Wherein R, R_1, R_2 are as hereinabove defined and R_4 is a C_1 to C_4 alkyl group, and

(ii) said quaternised amine is subsequently saponified with an aqueous base e.g. sodium hydroxide, to produce the betaine.

SURFACTANTS

The compositions of the present invention preferably contain at least 30% by weight of the amphoteric surfactant, preferably at least 33%, e.g. at least 35%, such as 45%, all percentages being based upon the total weight of said composition.

It is an especially preferred feature of the present invention that said betaine amphoteric surfactants are prepared from alkylamido dimethyl amines, alkyldimethylamines or fatty acid hydroxethyl imidazoline.

It is a preferred feature that any fatty imidazolines used comprise a C_8-C_{22} alkyl group, especially a C_{10}-C_{18} alkyl group, and a C_1 to C_4 hydroxyalkyl group, especially a C_2-C_3 hydroxyalkyl group. For example the fatty imidazoline derivatives may be derived from lauryl hydroxyethyl imidazoline.

REACTION MEDIUM

The organic solvents used to produce the reaction medium according to the present invention are non-surface active and miscible with water in some or all proportions.

Organic solvents suitable for use according to the present invention include water soluble monohydric alcohols e.g. C_1-C_4 monohydric alcohols; water soluble diols e.g. C_2-C_8 glycols such as ethylene glycol, propylene glycol, and hexylene glycol; water soluble polyglycols e.g. polyethylene glycol and polypropylene glycol; water soluble polyhydric alcohols e.g. glycerol, polyglycerols, and pentaerythritol; water soluble ethoxylated $C_{1 \text{ to } 4}$ alcohols, e.g. dipropylene glycol monomethylether.

Especially preferred organic solvents, according to the present invention, are propylene glycol, polyethylene glycol, dipropylene glycol monomethyl ether and/or glycerol.

The ratio of water-soluble, non-surface active organic solvent:water in said reaction medium is from 1:10 to 10:1, dependent upon the desired phase and viscosity of the resultant surfactant composition.

Said solvents may be present in the composition in a ratio of solvent: water such that the surfactant is present in an "L_1" phase or in a "G" phase. Typically an excess of solvent e.g. 60/40 w/w ratio of propylene glycol:water is required in the preparation of amphoteric surfactants, e.g. betaines, to produce a "G" phase, and an excess of water e.g. a 15/85 w/w ratio of propylene glycol:water is required in the preparation

of amphoteric surfactants, e.g. imidazoline derivatives, to produce an "L_1" phase, where in the absence of solvent an immobile or high viscosity composition would result.

Typically, said solvent is present in said composition at levels not exceeding 75%, usually between 5% and 65% based on the total weight of the composition, preferably 7%-40%. The percentage of said solvent, and its ratio to water, is adjusted according to the phase behaviour of the particular amphoteric surfactant, to provide a composition comprising essentially amphoteric surfactant, organic solvent and water, said composition being an "L_1" phase or a "G" phase at ambient temperature.

The level of reaction medium in the composition is typically greater than 35% by weight and less than 70% by weight of the composition, e.g. 40-65% dependent upon the nature of the active ingredients.

PREPARATION OF COMPOSITIONS

The compositions according to the present invention may be prepared by mixing an appropriate quantity of an amphoteric surfactant, which in the absence of the reaction medium according to the present invention would typically produce an immobile or high viscosity gel, with the correct proportion of water, and water miscible, non-surface active organic solvent, in order to obtain a surfactant composition in the "L_1" phase, or the "G" phase.

It is also possible to prepare the composition containing the active ingredients in a phase other than the "G" phase or "L_1" phase and adjust the water content of said composition by evaporation from, or diffusion into the mixture. The last method is not, however, usually practicable on an industrial scale.

Alternatively, the composition of the present invention may be prepared by the production of the amphoteric surfactant directly in the solvent/water medium, i.e. in situ. In such cases the proportions of solvent:water in said medium are sufficient to be capable of producing a composition in the "G" phase or "L_1" phase.

Carboxymethylation of amines to produce amphoteric surfactants

Frequently used carboxymethylation agents include those agents such a methyl acrylate, ethyl acrylate, acrylic acid, 2-hydroxy-1,3-propane sultone, 3-chloro-2-hydroxypropane sulphonic acid, 1,3-propane sultone, alkyl chloroacetate, and especially sodium chloroacetate. With the last, preferred carboxymethylating agent, alkylations may be carried out either neat, in inert solvents or, in aqueous solution.

Sufficient water should be present in the solvent medium to avoid the risk of substantially carboxymethylating the solvent.

Any suitable amount of carboxymethylating agent may be added to the reaction medium, typically being the minimum amount required to substantially carboxylate the amine.

The carboxylate may be neutralised to produce the amphoteric surfactant by treatment with any suitable neutralising agent, for example alkali or alkaline earth metal hydroxides e.g. NaOH.

The temperature of the carboxymethylation reaction may be between ambient and 120°C such that degradation of the amine or the amphoteric surfactant does not occur e.g. 35°C-90°C, especially 50°C-80°C.

The carboxymethylation reaction may be carried out over a period of 0.5 to 24 hours dependent upon the temperature of the reaction mixture and the degree of carboxymethylation required e.g. 5 to 20 hours, such as 12 to 18 hours.

Typically the reaction mixture may have a 10% aqueous solution pH of 7 to 14, e.g. 9 to 12.5, such as 10 to 12.

At the completion of the carboxymethylation reaction to produce an amphoteric surfactant composition, said composition typically has a solids content of 30-60% w/w, e.g. 35-55% and is either an "L_1" phase or "G" phase dependent upon the reaction medium employed and the active ingredients in question.

VISCOSITY CHARACTERISTICS

It is preferred that the compositions of the present invention, whilst being mobile, have a viscosity at ambient temperature such that they may be pumped at a rate sufficient to facilitate easy handling of the compositions.

Typically, the compositions of the present invention have viscosities in the range 400 to 15,000 centipose (cps), preferably 600 to 7000 cps, most preferably 700 to 6000 cps at ambient temperature.

Usually the composition is pumpable at concentrations within a range of $\pm$ 10%, active ingredient preferably $\pm$ 5% e.g. $\pm$ 2.5% of the minimum viscosity concentration. This range tends to be broader at more elevated temperatures.

The viscosity of compositions of the present invention may be determined by any suitable method e.g. Brookfield Viscometer or controlled shear/stress rheometer.

OPTIONAL INGREDIENTS

The compositions of the present invention may contain minor amounts of non-colloidal electrolytes such as sodium chloride or sodium sulphate. Such inclusions may be present as impurities from the feedstocks used during the manufacture of the component, or may be generated as by-products if the surfactant is manufactured in-situ. However, the presence of organic salts or similar non-colloidal electrolyte is undesirable, often resulting in an increase in the viscosity of the fluid "G" phase, and in the case of chloride salts may ultimately lead to problems of corrosion. We therefore prefer that the proportion of non-surface active electrolyte present in the compositions of the present invention is below 10% and more preferably below 5% by weight of the active mixture, preferably below 5% by weight of the total compositions. However, there are certain circumstances in which the presence of some electrolyte may be useful, e.g. when the melting point of the "G" phase is slightly above ambient temperature, and an increase in the electrolyte content of the composition may depress the melting point sufficiently to obtain a pumpable "G" phase without heating.

In such circumstances it may sometimes be desirable to deliberately add up to about 6% by weight of a non-colloidal electrolyte, e.g. sodium chloride, sodium sulphate, sodium acetate or sodium citrate.

The compositions of our invention may further optionally contain minor amounts, e.g. up to 5% by weight of the active mixture, of surface active material other than those specified herein.

USES OF THE AMPHOTERIC SURFACTANT COMPOSITIONS

Typically, the amphoteric surfactants of the present invention, may be formulated into surfactant compositions which may additionally comprise, for example, other surfactants or synergists, antiperspirants, deodorants, lanolin or other skin softening or moisturising preparation, analgesics, antiseptics, emulsifiers, dispersants, soaps, polymeric thickening agents, wetting agents, foam controlling agents, perfumes and colouring.

The amphoteric surfactants of the present invention are especially suitable for inclusion into the personal care products, where the mild nature of such surfactants is especially desirable.

EXAMPLES

The invention will be further illustrated by way of the following examples:-

Example 1 : The preparation of cocoamido propyl betaine (CAPB) in propylene glycol:water 60/40 w/w reaction medium

CAPB was prepared in-situ in a 60/40 w/w mixture of propylene glycol:water. Water (581.6g), propylene glycol (1556.4g), 80% aqueous monochloroacetic acid solution (781.2g), 47% aqueous NaOH solution (394.0g) and coco amidopropyl dimethylamine (2000.0g) were mixed and heated to 80°C. After the initial charging of the reactants, the pH of the reaction mixture was adjusted to 9.0 using NaOH solution (172.0g), with the reaction mixture being a clear, pale yellow liquid. No viscosity 'hump' characteristic of such preparations not using the reaction medium of the present invention was noted over this initial stage. The mixture was further heated at 80°C whilst maintaining the pH between 9.0-9.5 by addition of NaOH solution (100.0g in total)

As the reaction progressed, the mixture became increasingly turbid, especially at room temperature, with the mixture eventually becoming properly turbid at 50°C. The total reaction time was approximately 20 hours, with one addition of 80% monochloroacetic acid solution (7.5g) being made to lower the free amidoamine content. The pH of the final product was lowered to 5.1 by addition of $C.H_2SO_4$.

Analysis:

	% W/W
CAPB Active matter	40.2
Sodium chloride	7.0
Propylene glycol	30.7
Water	22.8
Free amidoamine	0.43
Sodium monochloroacetate	<25ppm
Free fatty acid	0.45
Sodium sulphate	0.30
Formaldehyde	0.03
Total active level (including salt)	47.2

The product was a mobile, free flowing "G" phase.

Example 2: The "in situ" Preparation of a Lauric Imidazoline derivative (CLHI) in 85/15 w/w water:propylene glycol reaction medium

In an appropriate vessel, 438g of lauric hydroxyethyl imidazoline was added to a reaction medium comprising an 391g water and 119g propylene glycol. 21g of 47% NaOH solution was added thereto.

To the reaction medium was added, as a carboxymethylating agent, 80% monochloroacetic acid (280g) and subsequently, as a neutralising agent, 47% NaOH (180g). The the reaction mixture was maintained at 70°C for 15 hours, and the pH of the reaction mixture was maintained by further addition of 47% NaOH Solution

The product was a clear, mobile amber coloured liquid with a total solids content of 50% by weight, being an L_1 phase at ambient temperature.

Finally, the pH of the reaction mixture was lowered to 10% aqueous solution pH 10.0 by the addition of 20g of C.HCI (36%), over a period of 1 hour, giving a total reaction time of approximately 22 hours.

Analysis of Product

Total Active Matter	33.5%
(of which:	
(Carboxymethylated amidoamine	32%)
(Noncarboxymethylated material	0.5%)
(Free fatty acid	1.0%)
	33.5
Sodium chloride	9.3%
Sodium monochloroacetate	<0.1%
Sodium glycollate	1.7%
Water (Karl-Fischer)	42.7%
Propylene glycol	7.1%
Total solids	50.2%

Viscosity (25°C, Brookfield, spindle #3, speed 10)	4100cps
pH (10% solution, 25°C)	10.3
Appearance	clear, mobile, pale amber solution.
Phase (25°C)	L1

The inclusion of propylene glycol (15:85 propylene glycol:water) in the initial charge yielded a product with a similar viscosity to a sample of a conventional carboxymethylated lauric hydroxy ethyl imidazoline derivative prepared in the absence of solvent, with the former having the advantage of a 39% w/w increase in solids content with an identical composition, on a "pro rata" basis.

Example 3: Preparation of amphoteric surfactants (I) in the absence of solvent

Samples of the lauric imidazoline derivative (I) prepared "in situ" according to the method of Example 2 in an aqueous reaction medium containing no water miscible organic solvent exhibited much higher viscosities at corresponding levels of solids than compositions produced in the presence of said solvent.

SOLIDS	VISCOSITY @ 25°C (Brookfield)
Lauric imidazaline 36 ± 2% solids (24.0-26.0% total actives)	5000 m.Pa.s
42 ± 2% solids	36000 m.Pa.s
50% solids	3725 m.Pa.s

The composition containing 50% solids exhibits an hexagonal M_1 phase structure at 25°C i.e. an immobile gel.

Example 4: Concentration and subsequent re-dilution of compositions of Example 2

Samples of the lauric imidazoline derivative composition of Example 3 were concentrated to 70-80% w/w solids by evaporation of water, and subsequently re-diluted to 50% w/w solids by the addition of mixtures of propylene glycol:water or glycerol:water co-solvents of various ratios.

After dilution and mixing was complete the phase viscosity at 25°C, 37°C and 45°C and the phase at ambient temperature of the compositions were determined.

Viscosity Determined Using a Controlled Shear/Stress Rheometer

% Solids	% Water	% Propylene Glycol	% Glycerol	Temp. deg.c	Viscosity cps
50	45	5	-	25	13,120
50	42.5	7.5	-	25	3,942
50	40	10	-	25	1,080
50	45	-	5	25	18,420
50	42.5	-	7.5	25	26,010
42	58	-	-	25	36,030
36	64	-	-	25	2,452
50	45	5	-	37	4,912
50	40	10	-	37	916
50	45	-	5	37	16,560
50	42.5	-	7.5	37	13,690
42	58	-	-	37	19,740
36	64	-	-	37	2,351
50	45	5	-	45	2,198
50	40	10	-	45	623
50	45	-	5	45	6,727
50	42.5	-	7.5	45	6,150
42	58	-	-	45	10,260
36	64	-	-	45	1,812

Measuring system used by controlled shear/stress rheometer

42cm 2^{o} cone & plate
Shear rate 8.51 s^{-1}

All of the compositions were clear L_1 phase solutions at ambient temperature, and exhibited no gel formation or phase separation upon dilution of the concentrated samples. The results suggest that the inclusion of glycerol is beneficial in reducing the viscosity of samples of the composition of Example 3, with the inclusion of propylene glycol being even more effective with regard to viscosity reduction.

Example 5 Preparation of Lauryl Amidopropyl Betaine (LAPB) in Propylene Glycol : Water 60:40 w/w Reaction Medium

LAPB was prepared in situ in a 60:40 w/w mixture of propylene glycol:water.

Water (450.8g), propylene glycol (1149.9g), 80% w/w aqueous monochloroacetic acid (MCA) solution (540.7g; 4.58mol), 47% w/w aqueous NaOH solution (272.7g; 3.20mol), and lauryl amidopropyl dimethylamine based on 99% C_{12} fatty acid (1300.0g; 4.58mol) were mixed together and heated to 80°C. The pH of the reaction mixture was raised to 9.0 by further addition of 47% w/w aqueous NaOH solution (119.0g; 1.40mol). The mixture was then stirred and heated at 80°C for 4 hours whilst maintaining the pH in the range of 9.0 to 9.5 by dropwise addition of NaOH solution. A further quantity of 80% w/w aqueous MCA (5.8g; 0.05mol) was added to lower the free amidoamine content, and the mixture was heated for another 20 hours at 80°C and at a pH of 9.0 to 9.5. The pH was lowered by addition of 36% w/w hydrochloric acid and the product cooled to ambient temperature. The overall mole ratio lauryl amidopropyl dimethylamine: MCA was 1.00:1.01.

The reaction mixture had the appearance of a clear, highly mobile, pale yellow solution throughout the charging, reaction, and neutralization steps. Analysis of the final products was as follows :

	w/w
LAPB Active Matter	40.8%
Total Solids	48.1%
Sodium Chloride	7.3%
Sodium Monochloroacetate	<80ppm
Free Amidoamine	0.2%
Free Fatty Acid	0.5%
Water	21.9%
Propylene Glycol	29.4%
Colour (Hazen)	70
pH (5% w/w solution at 25°C)	5.8
Viscosity (Brookfield; 24°C)	705 m.P.a.s.
Appearance at 25°C	Clear, mobile, pale yellow solution

The product remained stable during storage over three months at 3°C, at the end of which the appearance remained unchanged with no precipitation having occurred.

Example 6: The Preparation of LAPB in Dipropylene Glycol Monomethylether : Water 60:40 w/w Reaction Medium

LAPB was prepared in situ in a 60:40 w/w mixture of dipropylene glycol monomethylether:water.

Water (86.4g), dipropylene glycol monomethylether (223.5g) 80% w/w aqueous MCA solution (107.6g;0.91 mol), 47% aqueous NaOH solution (77.5g;0.91mol), and lauryl amidopropyl dimethylamine based on 99% C_{12} fatty acid (250.0g; 0.88mol) were mixed together and heated at 80°C.

The mixture was stirred and heated at 80°C for 4 hours whilst maintaining the pH in the range 9.0 to 9.5 by dropwise addition of NaOH solution. A further quantity of 80% w/w aqueous MCA (2.1g; 0.018mol) was added to lower the free amidoamine content, and the mixture was heated for another 16 hours at 80°C and at a pH of 9.0 to 9.5. The pH was lowered by addition of 36% w/w hydrochloric acid and the product cooled to ambient temperature. The overall mole ratio lauryl amidopropyl dimethylamine: MCA was 1.0:1.05.

The reaction mixture had the appearance of a mobile G-phase throughout the charging, reaction, and neutralization steps. Analysis of the final product was as follows :

Analysis

	w/w
LAPB Active Matter	41.0%
Total Solids	49.3%
Sodium Chloride	7.3%
Sodium Glycollate	0.4%
Sodium Monochloroacetate	<5ppm
Free Amidoamine	0.3%
Free Fatty Acid	0.3%
Water	23.4%
Dipropylene Glycol Monomethylether	27.3%
pH (5% w/w solution at 25°C)	6.0
Viscosity (15°C; 4cm 2°cone & Plate; shear rate 8.51 s^{-1})	3725mPa.s
Appearance at 25°C	mobile, pale yellow G phase solution

Example 7 The Preparation of Lauric Imidazoline Derivative in Water:Propylene Glycol 80:20 w/w Reaction Medium

Carboxymethylated lauric hydroxyethyl imidazoline derivative was prepared in situ in an 20:80 w/w propylene glycol:water mixture.

Lauric hydroxyethyl imidazoline (LHI) having 99% C_{12} content (268.0g; 1.00 mol) was added to a reaction medium comprising water (126.0g), propylene glycol (80.4g), and 47% w/w aqueous NaOH solution (12.8g; 0.15mol).

To the reaction mixture was added 80% w/w aqueous MCA solution (141.8g; 1.20 mol in total) and 47% w/w aqueous NaOH solution (111.9g; 1.31 mol in total). The mixture was then heated at 85°C for a further 15 hours whilst maintaining the pH by further addition of 47% w/w aqueous NaOH solution.

The reaction mixture was clear and highly mobile throughout the reaction, but became highly viscous on cooling, particularly below 55°C. A further quantity of solvent (164g) comprising 80:20 w/w water:propylene glycol was therefore added. The product was cooled to ambient temperature and the 10% solution pH adjusted to 10.0 by addition of 36% w/w hydrochloric acid.

Analysis

	w/w
Total Active	34.7%
Total Solids	48.6%
Ratio Active/Solids	71.4%
Noncarboxymethylated material	0.8%
Free Fatty Acid	1.4%
Sodium Chloride	7.3%
Sodium Monochloroacetate	<500ppm
Water	41.4%
Propylene Glycol	10.0%
pH (10% w/w solution at 25°C)	10.0
Viscosity (Brookfield at 25°C) spindle #3, speed 10 rpm))	1,40o m.Pa.s
Appearance at 25°C	clear, mobile, pale amber solution

Example 8 The Preparation of Coconut Imidazoline Derivative in Water:Propylene Glycol 80:20 w/w Reaction Mixture

Carboxymethylated coconut hydroxyethyl imidazoline derivative was prepared in situ in an 20:80 w/w propylene glycol:water mixture.

Coconut hydroxyethyl imidazoline (CHI) based on hardened coconut fatty acid (278g; 1.00 mol) was added to a reaction medium comprising water (198.0g), propylene glycol (91.3g), and 47% w/w aqueous NaOH solution (12.8g; 0.15 mol).

To the reaction mixture was added 80% w/w aqueous MCA solution (141.8g: 1.20 mol in total) and 47% w/w aqueous NaOH solution (109.8g: 1.29 mol in total). The mixture was heated at 85°C for a further 15 hours whilst maintaining the pH by further addition of 47% w/w aqueous NaOH solution.

The product was cooled to ambient temperature and the 10% solution pH adjusted to 8.8 by addition of 36% w/w hydrochloric acid, whereupon a precipitate of sodium chloride crystals formed. A further quantity of water (36g) was mixed with the product yielding a mobile, slightly turbid, amber solution free of solid precipitate.

Analysis

	w/w
Total Active	34.9%
Total Solids	53.4%
Noncarboxymetylated material	2.0%
Free Fatty Acid	1.4%
Sodium Chloride	9.9%
Sodium Monochloroacetate	<500ppm
Water	36.6%
Propylene Glycol	10.0%
pH (10% w/w solution at 25°C)	8.8
Viscosity (Brookfield at 25°C) spindle #3, speed 10 rpm))	2,150 m.Pa.s
Appearance at 25°C	turbid, mobile, pale amber solution

CLAIMS

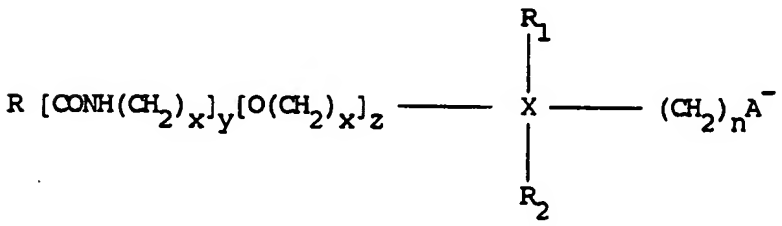
1. An amphoteric surfactant composition, consisting essentially of at least 5% and not more than 45% by weight of water; at least 30% by weight of amphoteric surfactant; and 5 to 45% of a water-miscible, non-surfactant organic solvent, wherein the concentration of surfactant in said composition corresponds to that at which the composition can exist, at least predominantly, in the "G" phase.

2. An amphoteric surfactant composition, consisting essentially of at least 5% and not greater than 65% by weight of water; at least 25% by weight of amphoteric surfactant; 5% to 45% of a water miscible, non-surfactant organic solvent, wherein said composition is an "L_1" phase.

3. A composition according to claim 1 consisting essentially of from 4 to 40% by weight water, 35 to 70% by weight of amphoteric surfactant and 5 to 45% by weight of said organic solvent.

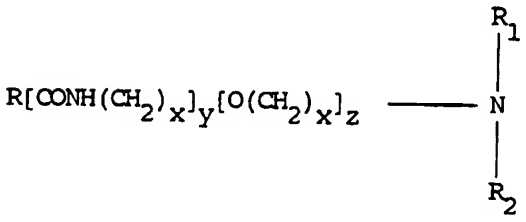
4. A composition according to claim 2 consisting essentially of 10% to 60% by weight, water, 30% to 70% by weight of amphoteric surfactant and 5 to 45% by weight of said solvent.

5. A composition according to any foregoing claim wherein the amphoteric surfactant comprises a compound of the formula:-



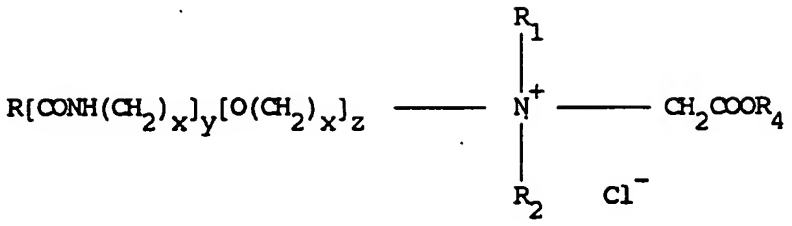
Wherein R is an alkyl, alkenyl, alkylamidoalkyl, alkenylamidoalkyl, alkyl polyoxyalkylene, alkenyl polyoxyalkylene or alkaryl group having in each case a C_{7-} C_{22} straight or branched chain alkyl or alkenyl group or may be combined with R_1 to form a cyclic group, x = 0 to 8, y = 0 or 1, z = 0 to 20, R^1 is H or a C_1-C_6 straight or branched chain alkyl, alkenyl or hydroxyalkyl group or may be combined with R or R_2 to form a cyclic group, R_2 is H or a C_1-C_6 straight or branched chain alkyl, alkenyl or hydroxyl group, or may be absent or may be combined with R_1 to form a cyclic group, X is nitrogen or phosphorus, n is from 1 to 3, and A is COO^-, SO_3^- or PO_3H^-.

6. A method for preparing a composition according to any foregoing claim by reacting a secondary or tertiary amine:-



wherein R, R_1 and R_2 are as defined in claim 5, with a carboxymethylating agent in the presence of the appropriate proportions of the non-surfactant water-miscible solvent and water.

7. A method according to claim 6 which comprises adding a chloroacetate ester to a secondary or tertiary amine to produce an ester of formula:



Wherein R, R_1, R_2 are as hereinabove defined and R_4 is a C_1 to C_4 alkyl group, wherein said quaternised amine is subsequently saponified with an aqueous base to produce a betaine.

8. A method according to either of claims 6 and 7 wherein said amphoteric surfactants are prepared from alkylamido dimethyl amines, alkyldimethylamines or fatty acid hydroxy ethyl imidazolamines.

9. A method according to claim 8 wherein said imidazoline comprises a C_8-C_{22} alkyl group, and a C_2-C_3 hydroxyalkyl group.

10. A method according to any of claims 6 to 9 wherein said solvent is propylene glycol, polyethylene glycol, dipropylene glycol monomethyl ether and/or glycerol.

11. A method according to any of claims 6 to 10 wherein the ratio of water-soluble, non-surface active organic solvent:water in said reaction medium is from 1:10 to 10:1.

INTERNATIONAL SEARCH REPORT

Inter[illegible]nal Application No
PCT[illegible] 94/03726

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/00 C11D3/43 C11D1/88 C11D1/90 C11D1/92
C11D11/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 426 731 (ALBRIGHT & WILSON) 21 December 1979 see the whole document	1,5

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search	Date of mailing of the international search report
15 March 1995	30. 03. 95
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Serbetsoglou, A

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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[illegible]/EP 94/03726

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